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(54) Chemiluminescent solution based on substituted anthracene

Chemilumineszente Lösung auf Basis von substituiertem Anthracen

Solution chimiluminescente à base d'anthracène substitué

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Description

The principle techniques for the production of chemiluminescent light have been described in great detail in U.S. Patent No. 4,678,608.

Chemiluminescence is produced by a reaction, in the liquid phase, of an activator such as hydrogen peroxide with a fluorescent agent and an oxalate. Optionally, other secondary compounds can be present such a catalysts, dyes etc.

Until recently, there existed no simple means for the production of pure blue chemiluminescent light to the satisfaction of the user, the conventionally used fluorescent dye to obtain a blue color being 9,10-diphenylanthracene. U.S. Patent 4,717,511 reveals, however, the use of a well-defined product, 9,10-bis(4-methoxyphenyl)-2-chloroanthracene, which produces a better light yield, as well as more pure blue color.

SUMMARY OF THE INVENTION

Unexpectedly, it has now been discovered that 9,10-bis(fluorophenyl)-2-fluoroanthracene or 9,10-bis(phenoxyphenyl)-2-chloroanthracene allow an equivalent or better yield of light emission (number of lumens-h/L) while at the same time still producing a similar, or even a more pure, blue color. Other advantages have also been observed, for example, with regard to the ease of synthesis and purification.

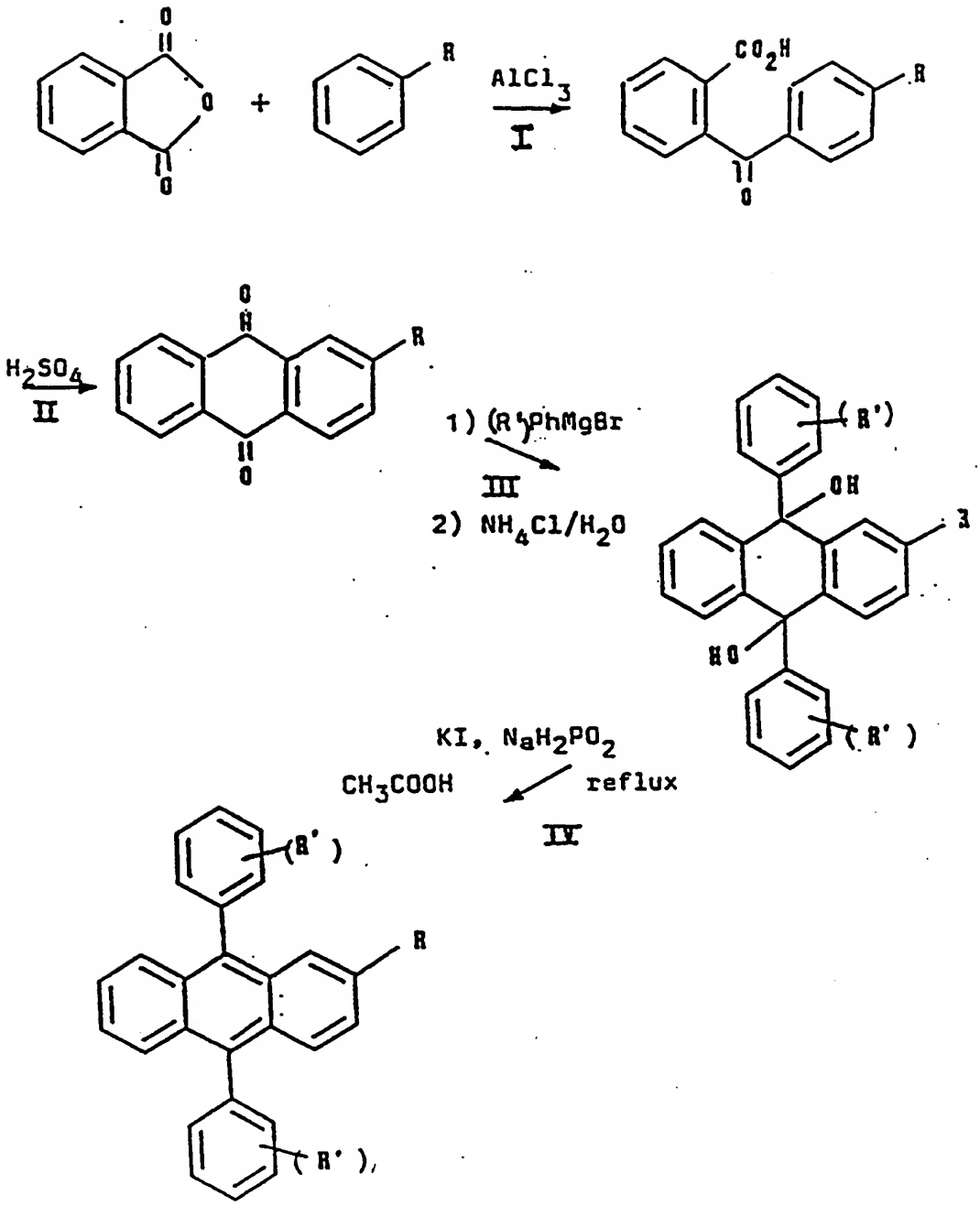
In addition, it has been observed that chemiluminescent solutions prepared with fluorescers which are derivatives of 9,10-diphenylanthracenes substituted according to the present invention, when mixed with a green chemiluminescent solution based on a conventional fluorescent dye 9,10-(bis(phenylethnyl)anthracene, unexpectedly produce solutions with a turquoise color which remains stable over time, a color which was not thought to be achievable before.

DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS

The new derivatives of anthracene according to the invention are prepared by a method, according to the reaction scheme given below, by aroylation of phthalic anhydride, with a 2-phenyl derivative under Friedel-Crafts reaction conditions i.e. using $AlCl_3$ followed by cyclization in, for example, sulfuric acid. The Grignard reagent, (R')nPhMgBR, is then added at 9,10 to the resultant anthraquinone and hydrolysis is then effected with ammonium chloride (C_1-C_4). The resultant hydrolyzed product is then reduced with potassium iodide, active acid and sodium hypophosphite under reflux conditions to form the resultant derivative which is isolated by filtering, washing with water, drying, dissolving in benzene and filtering after the addition of activated charcoal.

In the structural formulae, R represents a fluoro, chloro, bromo, alkoxy (C_1-C_4), or phenoxy subsitutent. (R')n represents one or more identical or different groups, said groups being alkoxy (C_1-C_4), phenoxy, fluoro, or polyalkylenoxy alkyl ether of 3-18 carbon atoms, n being 1-3, inclusive, except that when R is chloro, R' is not p-methoxy.

Reaction Scheme



The following examples are set forth for purposes of illustration only, except as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

Example A
(Substituted Anthraquinones)

1. Fluorobenzene is added to phthalic anhydride under Friedel-Crafts reaction conditions using $AlCl_3$ to produce the corresponding o-aroylbenzoic acid. The acid is cyclized with sulfuric acid to yield the corresponding anthraquinone which is then recrystallized from a 2:1 benzene/enthanol mixture. 2-Chloranthraquinone is commercially available.

Example B
(Anthracenediols)

0.2 Mol aliquots of the anthraquinones from Example A above, are each added slowly to the Grignard Reagent (R')-phenyl magnesium bromide, the R' being 4-fluoro and 4-phenoxy, respectively, (said Reagents having been produced by reacting one mole of R' phenylBr and 2 Mols of magnesium in 2 liters of dry tetrahydrofuran under a nitrogen atmosphere (excess magnesium being removed by filtration under nitrogen gas) and heated under reflux for 2 hours. The resultant reaction mixture is then hydrolyzed after cooling to room temperature with 200 ml of a 10% ammonium chloride solution. The tetrahydrofuran is evaporated off and the resultant residue is then extracted three times with 500 ml of hot benzene followed by drying over magnesium sulfate, filtering and evaporating again to produce the corresponding anthracenediols.

Example C
(9,10-Bisphenylanthracenes)

100 parts of each the anthracenediols of Example B are heated with reflex in 1500 mls. of glacial acetic acid for 5 hours with 200 parts of sodium iodide and 200 parts of sodium hypophosphite. The volume of acetic acid is brought to about 500 mls and one liter of water is then added to the reaction media. The resultant mixture is then filtered and washed 3 times with 500 mls. of water. After drying, the desired product is dissolved in benzene and filtered after the addition of activated charcoal. Solvent is eliminated in a rotary evaporator and the product is recrylstallized from a 1:1 benzene/ethanol mixture. After filtration, the crystals obtained are rinsed with 200 mls of ether and dried at 50°C for 10 hours and purified.

Examples 1 and 2

Utilizing the above procedures of Examples A-C, the following compounds are obtained, with the yields of anthracenediol and the final product being shown in parentheses:

Example 1

9,10-bis(4-fluorophenyl)-2-fluoroanthracene (78%, 80%)

Example 2

9,10-bis(4-phenoxyphenyl)-2-chloroanthracene (80%, 81%)

To produce chemiluminescence light, the compounds according to the present invention are used under the conditions already described in the literature, particularly in said U.S. Patent No. 4,678,608. In general, one can use any known solvent or oxalate which can be used for the production of chemiluminescent light. The solvent can be an ester, aromatic derivatives or a chlorinated hydrocarbon. Preferably, phthalates are used, in particular dibutyl phthalate.

Oxalates, such as those described in U.S. Patent No 3,749,679 may be used to produce the chemical reaction to cause chemiluminescent light when mixed with the fluorescers described above, with bis(2,4,5-trichloro-6-carbopentoxylphenyl) oxalate being exemplary. Substituted carbalkoxyphenyl oxalates are the preferred class of oxalates used herein, the oxalate and fluorescer each being used in sufficient quantity to cause chemiluminescent light, preferably in a 20-40:1 oxalate to fluorescer, molar ratio.

The blue fluorescer is used in amounts ranging from about 0.005 mole per liter of oxalate solution i.e. the solvent solution of the oxalate and the fluorescer.

Useful catalysts are disclosed in U.S. Patent No. 3,775,336 in concentrations disclosed therein, and usually in the solvent solution of the hydrogen peroxide.

The areas of application are well known and they include the production of useful objects, particularly signs, decorative objects, games and gadgets. In such articles, the chemiluminescent light is produced by mixing a solution of an

activator, in general oxygenated water (hydrogen peroxide), with a solution which contains the novel fluorescers hereof and an oxalate diester. The article consists of, in its passive state, two compartments between which a communicating is established at the time of use, for example as described in French Patent No. 87 11296, for the case of flexible luminescent tubes.

Example 3

a) Into a suitable vessel are charged 90 parts of 2,4,5-trichloro-6-carbopentoxyphenyl oxalate. The volume is increased with dibutyphthalate and heated to 150°C under nitrogen. While stirring, there is added approximately 1 part of the fluorescer of Example 1, when the temperature reaches 90°C.
b) 50 parts of 85% hydrogen peroxide are added to an 80/20 solution of dimethylphthalate/t-butanol, to bring the volume to 1L. Next, there is added 0.180 part of sodium salicylate.
c) The solutions prepared in a) and b) are then mixed in a volume proportion of 3 to 1. The result is a chemiluminescent emission of a particularly pure blue.

Example 4

Following the procedures of Example 3 except that the fluorescer of Examples 2 is used, similar results are obtained.

FURTHER EMBODIMENTS

In addition, it has been found that it is possible to produce compositions containing two fluorescers which are adapted to be reacted with hydrogen peroxide to provide chemiluminescent light of a color different than that emitted by either fluorescer alone. More particularly, a composition comprising a mixture of two fluorescers, each emitting a different color when used in a chemiluminescent composition, is prepared by mixing said fluorescers in amounts such as to produce a third color when the resultant composition is mixed with a peroxide. Specifically, the compounds described above emit a blue light upon activation with hydrogen peroxide in chemiluminescent systems. Similarly, the known fluorescer, 9,10-bis(phenylethynyl)anthracene emits a green light under the same conditions. However, when the blue and green fluorescers are blended into a composition, the color emitted by activation with hydrogen peroxide is turquoise. Similarly, a red fluorescer can be blended with the blue fluorescer hereof to give pink. The red fluorescer of our copending U.S. Patent No. 5,122,306 can be used for this purpose. This feature forms part of the scope of the invention set forth herein. The shade of the different color achieved can be attained by varying the concentration of either fluorescer. Thus, from about 95:5 to about 5:95 parts of either fluorescer can be used.

Example 5

A solvent solution of the blue fluorescer of Example 1 is mixed with 1,6,7,12-tetraphenoxy-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide in a ratio of 73:27. The color emitted is turquoise.

Claims

Claims for the following Contracting States : AT, BE, CH, DE, DK, FR, GB, LI, NL, SE

1. A compound selected from the group consisting of 9,10-bis(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-Chloroanthracene.

2. A composition adapted to be reacted with hydrogen peroxide to provide chemiluminescent light, said composition containing a compound of claim 1.

3. A composition according to claim 2 further comprising a solvent for said compound.

4. A composition according to claim 2 further comprising an oxalate compound.

5. A composition according to claim 4 wherein said oxalate compound is a substituted carbalkoxyphenyl oxalate.

6. A composition according to claim 5 wherein said oxalate is bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate.

7. A composition according to claim 3 wherein said solvent is dibutylphthalate.

8. A method of producing chemiluminescent light which comprises adding to the composition of claim 4, a solution of hydrogen peroxide.

Claims for the following Contracting State : ES

1. A process for producing a composition adapted to be reacted with hydrogen peroxide to provide chemiluminescent light, said process comprising the step of mixing a compound selected from the group consisting of 9,10-bis(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-chloroanthracene and a solvent for said compound.

2. A process for producing a composition adapted to be reacted with hydrogen peroxide to provide chemiluminescent light, said process comprising the step of mixing a compound selected from the group consisting of 9,10-bis(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-chloroanthracene and an oxalate compound.

3. The process according to claim 2 wherein said oxalate compound is a substituted carbalkoxyphenyl oxalate.

4. The process according to claim 3 wherein said oxalate is bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate.

5. A process according to claim 1 wherein said solvent is dibutylphthalate.

6. A method of producing chemiluminescent light which comprises adding to the composition of claim 4, a solution of hydrogen peroxide.

7. Use of a compound selected from the group consisting of 9,10-bis(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-chloroanthracene for producing a composition adapted to be reacted with hydrogen peroxide to produce chemiluminescent light.

Claims for the following Contracting State : GR

1. A composition adapted to be reacted with hydrogen peroxide to provide chemiluminescent light, said composition containing a compound selected from the group consisting of 9,10-bis-(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-chloroanthracene.

2. A composition according to claim 1 further comprising a solvent for said compound.

3. A composition according to claim 1 or 2 further comprising an oxalate compound.

4. A composition according to claim 3 wherein said oxalate compound is a substituted carbalkoxyphenyl oxalate.

5. A composition according to claim 4 wherein said oxalate is bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate.

6. A composition according to claim 2 or 3 wherein said solvent is dibutylphthalate.

7. A method of producing chemiluminescent light which comprises adding a solution of hydrogen peroxideto the composition of claim 3.

8. Use of a compound selected from the group consisting of 9,10-bis(fluorophenyl)-2-fluoroanthracene and 9,10-bis(phenoxyphenyl)-2-chloroanthracene for producing a composition adapted to be reacted with hydrogen peroxide to produce chemiluminescent light.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, DK, FR, GB, LI, NL, SE

1. Verbindung, ausgewählt aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxphenyl)-2-chloranthracen.

2. Zusammensetzung zur Umsetzung mit Wasserstoffperoxid zur Schaffung chemilumineszenten Lichtes, die eine Verbindung nach Anspruch 1 enthält.

3. Zusammensetzung nach Anspruch 2, weiter umfassend ein Lösungsmittel für diese Verbindung.

4. Zusammensetzung nach Anspruch 2, weiter umfassend eine Oxalat-Verbindung.

5. Zusammensetzung nach Anspruch 4, worin die Oxalat-Verbindung ein substituiertes Carbalkoxyphenyloxalat ist.

6. Zusammensetzung nach Anspruch 5, worin das Oxalat Bis(2,4,5-trichlor-6-carbopentoxyphenyl)oxalat ist.

7. Zusammensetzung nach Anspruch 3, worin daS Lösungsmittel Diburylphthalat ist.

8. Verfahren zum Herstellen chemilumineszenten Lichtes, umfassend die Zugabe einer Lösung von Wasserstoffperoxid zur Zusammensetzung nach Anspruch 4.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zum Herstellen einer Zusammensetzung zum Umsetzen mit Wasserstoffperoxid zum Erzeugen chemilumineszenten Lichtes, wobei das Verfahren die Stufe des Vermischens einer Verbindung, die ausgewählt ist aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxyphenyl)-2-chloranthracen, und eines Lösungsmittels für diese Verbindung umfaßt.

2. Verfahren zum Herstellen einer Zusammensetzung zum Umsetzen mit Wasserstoffperoxid zum Erzeugen chemilumineszenten Lichtes, wobei das Verfahren die Stufe des Vermischens einer Verbindung, die ausgewählt ist aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxyphenyl)-2-chloranthracen, und einer Oxalatverbindung umfaßt.

3. Verfahren nach Anspruch 2, worin die Oxalatverbindung ein substitutiertes Carbalkoxyphenyloxalat ist.

4. Verfahren nach Anspruch 3, worin das Oxalat Bis(2,4,5-trichlor-6-carbopentoxyphenyl)oxalat ist.

5. Verfahren nach Anspruch 1, worin das Lösungsmittel Dibutylphthalat ist.

6. Verfahren zum Erzeugen chemilumineszenten Lichtes, umfassend die Zugabe einer Lösung von Wasserstoffperoxid zu der Zusammensetzung von Anspruch 4.

7. Verwendung einer Verbindung, die ausgewählt ist aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxyphenyl)-2-chloranthracen, zum Herstellen einer Zusammensetzung zum Umsetzten mit Wasserstoffperoxid zum Erzeugen chemilumineszenten Lichtes.

Patentansprüche für folgenden Vertragsstaat : GR

1. Zusammensetzung zum Umsetzen mit Wasserstoffperoxid zum Erzeugen chemilumineszenten Lichtes, wobei die Zusammensetzung eine Verbindung enthält, die ausgewählt ist aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxyphenyl)-2-chloranthracen.

2. Zusammensetzung nach Anspruch 1, weiter umfassend ein Lösungsmittel für die Verbindung.

3. Zusammensetzung nach Anspruch 1 oder 2, weiter umfassend eine Oxalatverbindung.

4. Zusammensetzung nach Anspruch 3, worin die Oxalatverbindung ein substituiertes Carbalkoxyphenyloxalat ist.

5. Zusammensetzung nach Anspruch 4, worin das Oxalat Bis(2,4,5-trichlor-6-carbopentoxyphenyl)oxalat ist.

6. Zusammensetzung nach Anspruch 2 oder 3, worin das Lösungsmittel Dibutylphthalat ist.

7. Verfahren zum Erzeugen chemilumineszenten Lichtes, umfassend die Zugabe einer Lösung von Wasserstoffper-

oxid zu der Zusammensetzung von Anspruch 3.

8. Verwendung einer Verbindung, die ausgewählt ist aus der Gruppe bestehend aus 9,10-Bis(fluorphenyl)-2-fluoranthracen und 9,10-Bis(phenoxyphenyl)-2-chloranthracen zum Herstellen einer Zusammensetzung zum Umsetzen mit Wasserstoffperoxid zum Erzeugen chemilumineszenten Lichtes.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, DK, FR, GB, LI, NL, SE

1. Composé choisi dans le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroanthracène.

2. Composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente, ladite composition contenant un composé de la revendication 1.

3. Composition selon la revendication 2 comprenant, en outre, un solvant dudit composé.

4. Composition selon la revendication 2 comprenant, en outre, un composé oxalate.

5. Composition selon la revendication 4, dans laquelle ledit composé oxalate est un oxalate de carbalcoxphényle substitué.

6. Composition selon la revendication 5, dans laquelle ledit oxalate est l'oxalate de bis(2,4,5-trichloro-6-carbopentoxyphényle).

7. Composition selon la revendication 3, dans laquelle ledit solvant est le phtalate de dibutyle.

8. Procédé de production d'une lumière chimioluminescente qui comprend l'addition à la composition de la revendication 4 d'une solution de peroxyde d'hydrogène.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de production d'une composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente, ledit procédé comprenant l'étape consistant à mélanger un composé choisi dans le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroanthracène et un solvant dudit composé.

2. Procédé de production d'une composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente, ledit procédé comprenant l'étape consistant à mélanger un composé choisi dis le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroathracène et un composé oxalate.

3. Procédé selon la revendication 2, dans lequel ledit composé oxalate est un oxalate de carbalcoxyphényle substitué.

4. Procédé selon la revendication 3, dans lequel ledit oxalate est l'oxalate de bis(2,4,5-trichloro-6-carbopentoxyphényle).

5. Procédé selon la revendication 1, dans laquelle ledit solvant est le phtalate de dibutyle.

6. Procédé de production d'une lumière chimioluminescente qui comprend l'addition à la composition de la revendication 4 d'une solution de peroxyde d'hydrogène.

7. Utilisation d'un composé choisi dis le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroanthracène pour produire une composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente.

Revendications pour l'Etat contractant suivant : GR

1. Composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente, ladite composition contenant un composé choisi dans le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroanthracène.

2. Composition selon la revendication 1 comprenant, en outre, un solvant dudit composé.

3. Composition selon la revendication 1 ou 2 comprenant, en outre, un composé oxalate.

4. Composition selon la revendication 3, dans laquelle ledit composé oxalate est un oxalate de carbalcoxyphényle substitué.

5. Composition selon la revendication 4, dans laquelle ledit oxalate est l'oxalate de bis(2,4,5-trichloro-6-carbopentoxyphényle).

6. Composition selon la revendication 2 ou 3, dans laquelle ledit solvant est le phtalate de dibutyle.

7. Procédé de production d'une lumière chimioluminescente qui comprend l'addition à la composition de la revendication 3 d'une solution de peroxyde d'hydrogène.

8. Utilisation d'un composé choisi dans le groupe constitué par le 9,10-bis(fluorophényl)-2-fluoroanthracène et le 9,10-bis(phénoxyphényl)-2-chloroanthracène pour produire une composition conçue pour réagir avec du peroxyde d'hydrogène pour donner une lumière chimioluminescente.